

DETERMINATION OF HYDROXYL CONTENT OF COALS BY THE
FORMATION OF TRIMETHYLSILYL ETHERS

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Abstract

Although a number of methods for determining hydroxyl groups in coal have been used, a more reliable and independent method is needed to correlate and check the results obtained in various laboratories. This paper presents a new method for the determination of hydroxyl groups in coal based on the formation of trimethylsilyl ethers, $\text{ROSi}(\text{CH}_3)_3$, by treating coal with hexamethyldisilazane, $(\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)_3$ and trimethylchlorosilane, $(\text{CH}_3)_3\text{SiCl}$, in pyridine at about 115°C . The resulting derivatives are analyzed for silicon to calculate the hydroxyl content in the coal samples. Experiments on model compounds have shown that hydroxycarbonyl compounds and even highly hindered phenols (2,6-di-*t*-butylphenol) form trimethylsilyl ethers quantitatively under reaction conditions.

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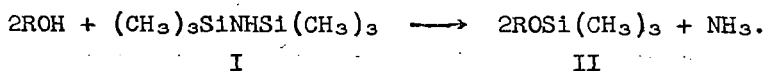
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Introduction

Although a number of methods have been used for determining hydroxyl groups in coals,* a more reliable and independent method is needed for correlating and checking the results of various laboratories. This paper presents preliminary work on the determination of hydroxyl groups in coal by the formation of their trimethylsilyl ethers. The method appears to offer an excellent way for determining the hydroxyl content of coals as well as providing a means for introducing a protective group which is easily removed.

Work in these laboratories has shown that hexamethyldisilazane (I) reacts quantitatively with hydroxyl groups, including even the most hindered ones, according to the following equation (1):



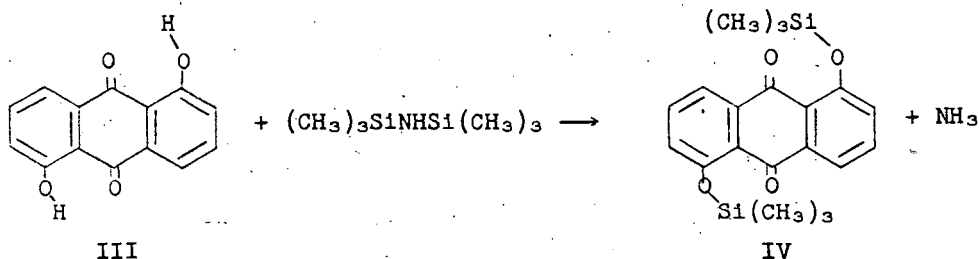
The resulting trimethylsilyl ether (II) is thermally stable and resistant to oxidation. The starting compound, however, is easily recovered from the ether by hydrolysis.

This reagent was first used for quantitative determination of hydroxylated compounds in the analysis of mixtures of Fischer-Tropsch alcohols, by mass-spectrometric analysis of their trimethylsilyl ethers (2). The mixture of ethers was more easily analyzed than the original alcohol mixtures. Reaction between these aliphatic alcohols and reagent (I) was rapid and quantitative.

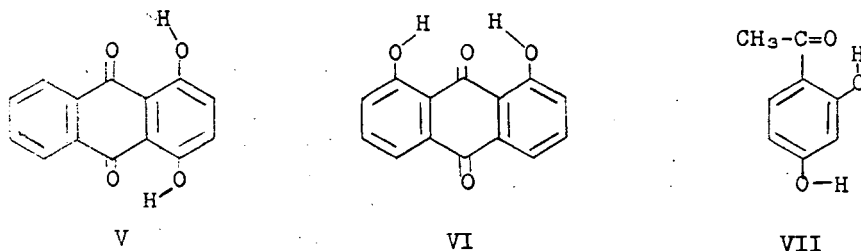
The reaction was equally adaptable to simple phenols; this prompted an investigation into its use for hydroxyl groups present in hydrogen-bonded hydroxycarbonyl compounds such as 1,5-dihydroxyanthraquinone (III). Hydrogen-bonded quinone groupings such as are found in this compound have been postulated to exist also in coal (3,4). This compound is reported to form a dimethyl ether only under rather severe

*/ For a review of these methods, see reference 6.

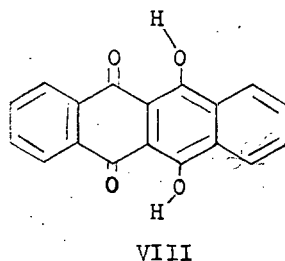
reaction conditions (5); i.e., when its dipotassium salt is heated with dimethyl sulfate at 140°C. It forms a bis(trimethylsilyl)ether (IV) readily on refluxing in hexamethyldisilazane; the reaction is essentially quantitative.



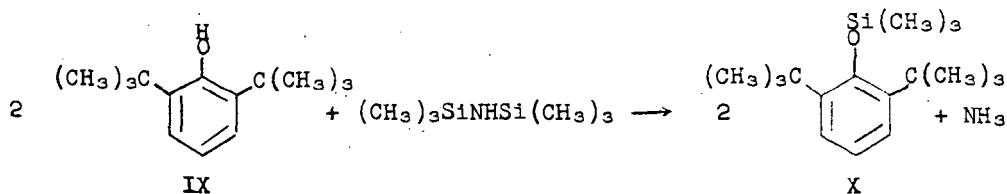
The related 1,4- and 1,8-dihydroxyanthraquinones (V, VI) as well as the hydrogen-bonded keto-phenol, 2,4-dihydroxyacetophenone (VII), also react readily to form trimethylsilyl ethers.



The compound 6,11-dihydroxynaphthacene-9,10-quinone (VIII), which is similar to 1,4-dihydroxyanthraquinone, was found to acetylate to the extent of only 10 percent, and methylate to the extent of 5 percent (6).



Further work has demonstrated that a highly-hindered phenol, 2,6-di-*t*-butylphenol (IX), reacts quantitatively with hexamethyldisilazane in the presence of trimethylchlorosilane and pyridine to form a stable trimethylsilyl ether (X) which can be used as a derivative of the phenol.



Reported attempts to form other derivatives of this hindered phenol indicate that it is necessary to form the sodium salt in liquid ammonia first before any reaction will take place (7). Thus, even in the case of a hindered phenol, reaction with hexamethyldisilazane represents a convenient and quantitative method for the formation of a derivative.

The same procedure has been applied to a series of coals, with the formation of the trimethylsilyl ethers of the hydroxyl groups in the coals. The derivatives have been analyzed for silicon to calculate the percentage of hydroxyl in the original coal.

Experimental Procedures and Results

Preparation of Trimethylsilyl Ether of 1,5-Dihydroxyanthraquinone

To 15 ml. of hexamethyldisilazane was added 2.5 g. of 1,5-dihydroxyanthraquinone (recrystallized, melting point 280°-284°C.) and one drop of trimethylchlorosilane. The mixture was refluxed for 24 hours. Hexamethyldisilazane and other relatively volatile substances were distilled off under vacuum, leaving 2.6 g. of solid which was recrystallized from petroleum ether (b.p. 60-68). The orange crystals, m.p. 138-142°C., had an infrared spectrum with absorption bands at 8.0, 9.45, 11.80, and 13.25 μ , all of which have been found to be common to phenyl trimethylsilyl ethers. In addition, the band at 12.70 μ , found in phenols, was absent, and the 6.12 and 6.23 μ bands of 1,5-dihydroxyanthraquinone, due to hydrogen-bonded carbonyl and aromatic absorptions, were shifted to 5.9 and 6.12 μ in the bis(trimethylsilyl)ether. These spectra are shown in Figure 1.

Analysis of the ether:

Calcd. for $\text{C}_{20}\text{H}_{24}\text{O}_4\text{Si}$	C, 62.46;	H, 6.29
Found	C, 62.81;	H, 6.45

Preparation of Trimethylsilyl Ethers of Other Hydrogen-bonded Hydroxy-carbonyl Compounds

By the same procedure derivatives were prepared from 1,8-dihydroxyanthraquinone, 1,4-dihydroxyanthraquinone and 2,4-dihydroxyacetophenone. The infrared spectra of the last two compounds and their derivatives, Figures 2 and 3, showed the same changes in spectra which were noted in the case of the 1,5-dihydroxyanthraquinone.

Preparation of Trimethylsilyl Ether of 2,6-di-t-butylphenol

A 10 g. sample of 2,6-di-t-butylphenol was refluxed for 24 hours with 5 ml. of hexamethyldisilazane and 10 ml. of trimethylchlorosilane in 25 ml. of dry pyridine. Ammonium chloride sublimed into the condenser and the color of the solution changed from pale yellow to light pink during refluxing. Solvent and unreacted reagents were distilled off under vacuum, leaving 10.3 g. of straw-colored crystals which were recrystallized from petroleum ether (b.p. 60-68°). A second recrystallization gave colorless crystals of m.p. 109-110°C.

Calcd. for $C_{17}H_{30}SiO$	C, 73.31;	H, 10.86
Found	C, 73.30;	H, 10.90.

The infrared spectrum showed the complete disappearance of the hydroxyl band at 2.9μ and bands appeared at 8.0, 9.5, 11.8, and 13.25μ as in the other phenyl trimethylsilyl ethers. There were also other changes in the spectrum due to skeletal vibrations. The spectra are shown in Figure 4.

Unsuccessful attempts were made to prepare this trimethylsilyl ether with hexamethyldisilazane and trimethylchlorosilane without pyridine, trimethylchlorosilane and pyridine without hexamethyldisilazane, and hexamethyldisilazane and pyridine with only a drop of trimethylchlorosilane as catalyst; a trace of ether was found in the last case.

Formation of Trimethylsilyl Ethers of Coal Hydrogenation Asphaltene

To 20 ml. of hexamethyldisilazane was added 1.0 g. of coal hydrogenation asphaltene and one drop of trimethylchlorosilane. The solution was refluxed under nitrogen for 3 days, and then the reagents were distilled off under vacuum. As the dry residue was somewhat soluble in heptane, it could not be washed. Instead, the product was vacuum oven-dried to constant weight. Infrared analysis indicated that essentially all hydroxyl groups had reacted.

Analysis of asphaltene before treatment: C, 85.25;
H, 7.00; N, 1.15; O, 6.60.

The treated asphaltene contained 6.21% silicon, corresponding to a hydroxyl content equivalent to 64% of the oxygen present in the original asphaltene.

Formation of Trimethylsilyl Ethers of Coals

Reflux method. A 5 g. sample of the coal, ground to -325 mesh and dried to constant weight in a vacuum oven, was refluxed under nitrogen in a solution of 5 ml. of trimethylchlorosilane and 10 ml. of hexamethyldisilazane in 50 ml. of dry pyridine. Except where noted (Table 2), the reflux period was 4 days. At the end of this time, the reagents were distilled off under vacuum. The reacted coal was washed with petroleum ether (b.p. 60-68°) to remove the last traces of reagents and dried in a vacuum oven. Original ultimate analyses, silicon determinations, and calculated percentages of hydroxyl in the coals,

Table 1.- Trimethylsilyl ether formation of coals.

Coals	Percent, moisture- and ash-free basis				Percent silicon in original coal	Percent hydroxyl oxygen in original coal		Percent OOH total		
	Carbon	Hydro- gen	Nitro- gen	Sulfur						
Colorado, Weld County	66.91	5.48	1.41	0.39	25.81	4.22	0.93	6.81	4.13	16.0
Alberta, Red Hot Mine, Edmonton	70.75	5.32	1.41	3.35	19.14	10.54	1.36	10.64	7.79	40.7
Illinois, Little Dog Mine	71.94	5.50	1.36	2.71	18.58	8.58	3.13	8.04	3.51	18.9
Jugoslavica, Rasez	75.06	5.58	1.13	12.14	6.09	12.58	0.51	2.47	1.35	22.2
Illinois, Little John Mine, Knox County	76.47	5.66	1.38	3.35	13.13	7.42	1.57	8.80	5.15	39.2
Ohio, Dorothy Mine, Belmont County	77.42	5.47	1.36	4.18	11.57	4.18	1.42	6.71	3.81	32.9
Ohio, Hocking #6 Bed, Athens	77.52	5.33	1.59	1.07	14.48	6.92	1.53	7.74	4.53	31.3
Kentucky #11 Seam, Hopkins County	77.94	5.68	1.58	3.70	11.11	5.46	1.26	8.09	5.21	46.9
Kentucky, #12 Seam, Hopkins County	78.00	5.79	1.39	3.71	11.10	10.90	2.98	9.38	5.41	48.7
Indiana, #5 Red, Enos	78.15	5.74	1.54	3.82	10.74	9.05	1.98	8.38	4.78	44.5
Kentucky, #11 Seam, Muhlenberg County	78.37	5.62	1.60	3.56	10.00	7.87	2.11	7.05	5.61	56.1
Indiana, #5 Seam, Knox County	78.79	5.72	1.57	4.37	9.55	7.68	1.47	8.47	5.26	55.1
Illinois, #6 Seam, Jefferson County	78.87	5.57	1.83	1.47	12.24	7.06	2.03	8.94	5.34	43.6
Wyoming, Rock Springs	79.31	5.41	1.74	0.90	12.65	1.96	0.48	6.89	4.47	35.3
Utah, Sunnyside #1, Carbon County	79.79	5.73	1.74	1.01	11.72	5.42	1.86	6.98	3.56	30.4
Illinois, #5 Seam, Saline County	80.90	5.62	1.92	1.32	10.25	6.71	1.80	8.90	4.68	45.6
West Virginia, #8 Bed, Marion County	82.32	5.70	1.27	3.69	6.88	8.91	1.63	5.91	3.23	46.9
Pennsylvania, Princeton	82.68	5.51	1.61	1.18	9.02	4.93	1.17	6.17	3.45	38.2
West Virginia, #2 gas bed, Lady Dunn Mine	84.93	5.65	1.71	0.82	6.79	3.36	0.83	5.61	3.22	47.4
West Virginia, #8 Bed, Big Knob #A.	87.86	5.20	1.17	1.01	4.77	7.52	1.65	4.35	1.79	37.5
Pennsylvania, Jedo Anthracite	93.25	2.23	0.79	0.52	1.26d/	3.34	0.70	0.99	0.18	14.3
Pennsylvania, Bruceton anthracite ^{a/b}	83.25	5.50	1.56	0.69	9.00	1.22	0.37	5.78	3.63	40.3
								5.78	3.36	46.3
								5.61	3.54	39.3

a/ Not in graph.

b/ Refluxed with water for 1 hour, dried, then treated.

c/ Reacted in bomb at 150°C.

d/ Direct oxygen determination.

based on the uptake of silicon, are shown in Table 1. Some of the data are also shown in Figures 5 and 6.

Pretreating coal (Bruceton anthraxylon) with boiling water had no effect on the determinable hydroxyl content (Table 1).

In more recent work reflux periods from 1 hour to 8 days were tried on one coal. As shown in Table 2, the reaction was essentially complete after only 1 hour. With this coal (14.5% O) the method was precise to $\pm 3\%$ of the oxygen content, based on the weight of total oxygen in the moisture- and ash-free coal.

Table 2.- Effect of time on formation of trimethylsilyl ethers in coal from Hocking #6 bed, Athens, Ohio.

Time, hours	Silicon in treated coal, %	Oxygen as OH in original coal, %	$\frac{O_{OH}}{O_{total}}$, %
1	8.08	5.07	35.0
4	7.97	4.97	34.3
24	8.35	5.33	36.8
96	7.90	4.60	31.8
96	7.57	4.91	33.9
192	8.57	5.43	37.5
Average	8.07	5.05	34.9

Bomb method. In a small stainless steel bomb (volume, 70 ml.) 4.861 g. of Bruceton anthraxylon, 5 ml. each of trimethylchlorosilane and hexamethyldisilazane, and 17 ml. of pyridine were heated to 150°C. for 5 hours. The product was treated as in the reflux method. Results are included in Table 1.

As the bomb method at elevated temperature did not increase the number of trimethylsilyl groups introduced into Bruceton anthraxylon, it showed that the reaction had been rapidly completed at reflux temperature in pyridine.

Silicon Analysis

Silicon was determined by peroxide bomb fusion of the samples, followed by treatment of residues with hydrofluoric acid to volatilize silicon. The analyses, done in duplicate, checked to within $\pm 0.1\%$.

Discussion

A recent article by Blom, Edelhausen, and Van Krevelen (6) reviews the various methods used for determining hydroxyl groups in coals. The uncertainties in each of these methods indicate the need for a more reliable method. Methylation by methyl sulfate in base (8) and by diazomethane (6) gives low values, presumably due to incomplete reaction. Ion-exchange, with barium hydroxide (9) may give rise to hydrolysis products and appears to suffer because of inaccessibility in high-rank coals. Potentiometric titration in ethylenediamine (10, 11) determines not only the acidic hydroxyl, but also such groups as quinones and acidic non-hydroxylic hydrogen; this method is also difficult to reproduce. Different procedures have been tried for acetylation as well as for estimating the extent of reaction (6, 12, 13, 14); each worker has reported different values for similar rank coals. The sources of these variations in results are still unexplained.

Comparison of the data in Table 1 and Figures 5 and 6 with published values shows the present ones to be higher than those found by methylation (6, 8), lower than those found by acetylation (6) and ion-exchange (9), and similar to those determined by titration (10, 11) and acetylation (12, 13, 14). Most of the other methods are indirect, and either known side reactions or difficulties in completing the reaction throw doubt on the reliability of the results. On the other hand, the present method is easy and direct, has no known side reactions, and is complete even where other reagents fail altogether.

As concerns the structure of coal, the ease of ether formation may indicate that few highly hindered phenolic groups, such as in 2,6-di-*t*-butylphenol, are present, since this phenol required 24 hours for complete reaction.

Acknowledgments

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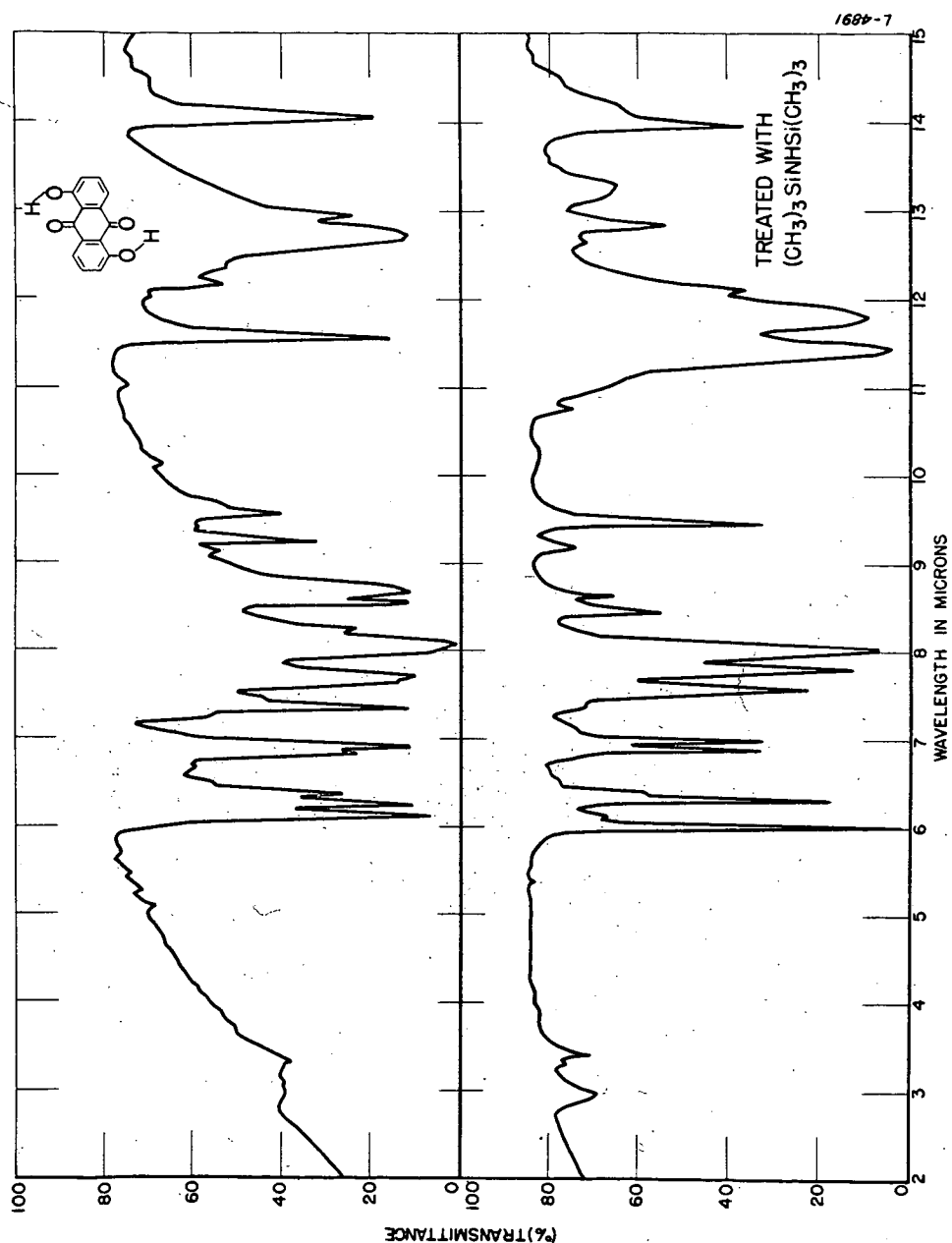


Figure 1 - Infrared spectra of 1,5-dihydroxyanthraquinone and its silyl ether.

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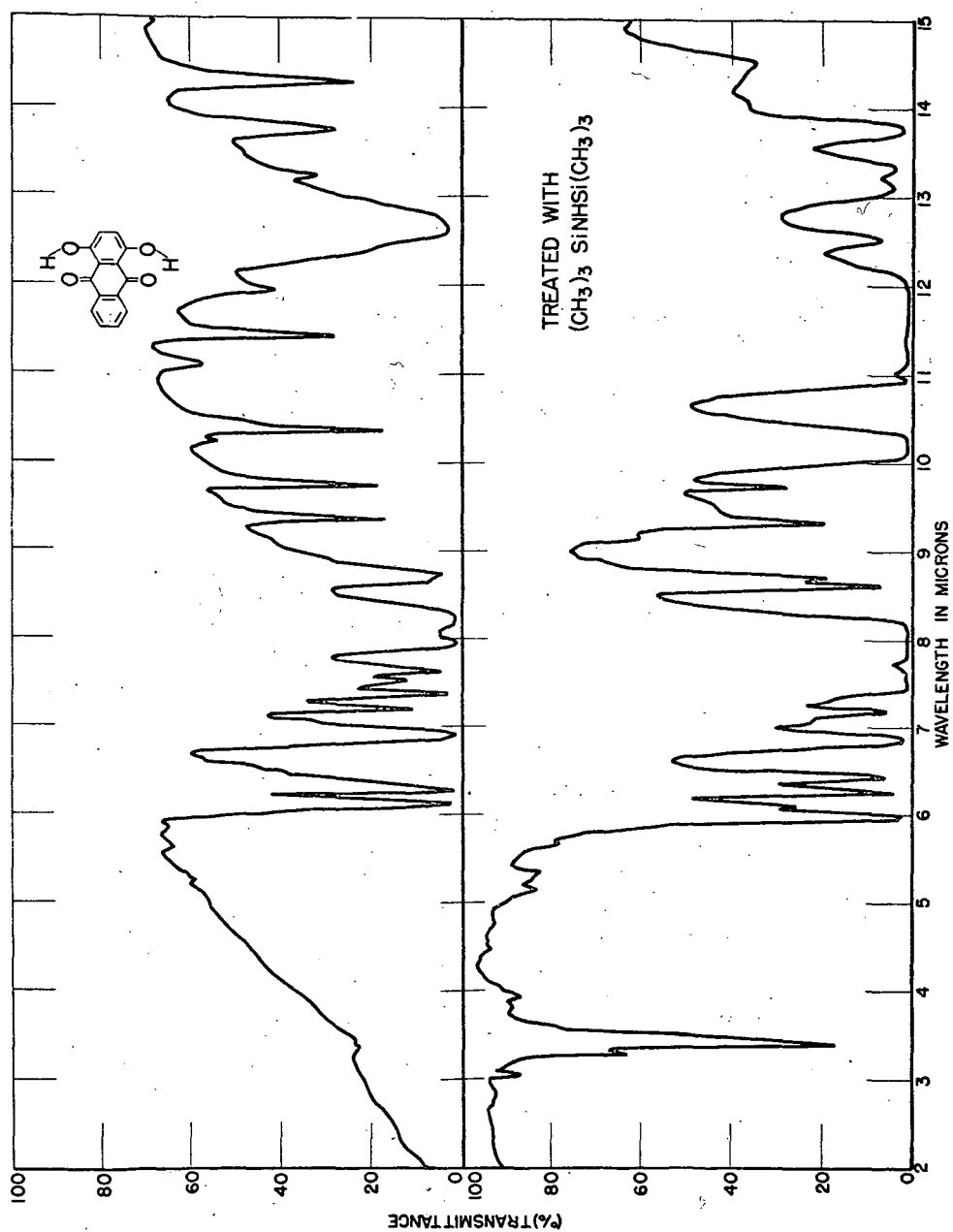


Figure 2.- Infrared spectra of 1,4-dihydroxyanthraquinone and its silyl ether

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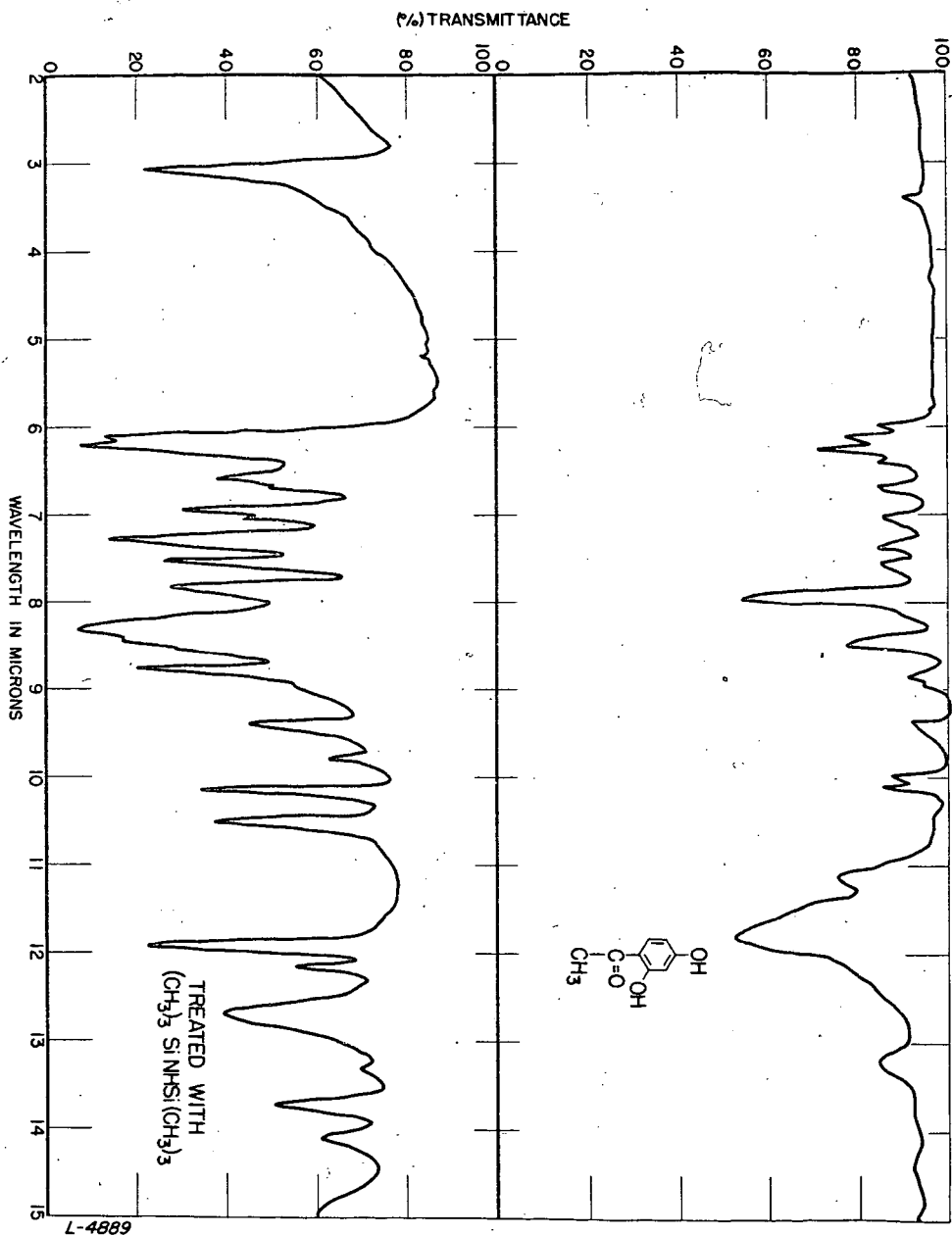


Figure 3.- Infrared spectra of 2,4-dihydroxyacetophenone and its silyl ether.

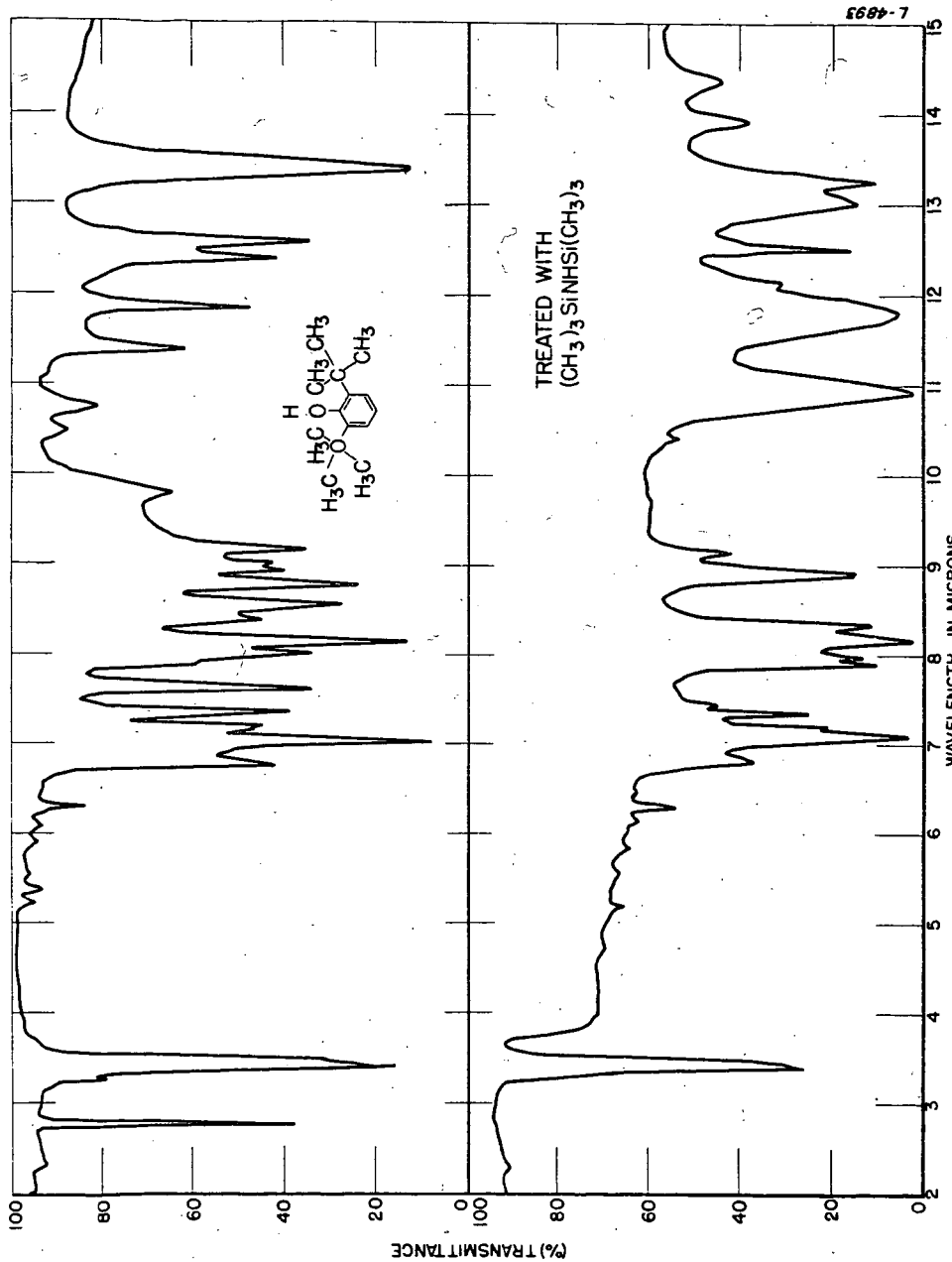


Figure 4.- Infrared spectra of 2,6-di-1-butylphenol and its silyl ether.

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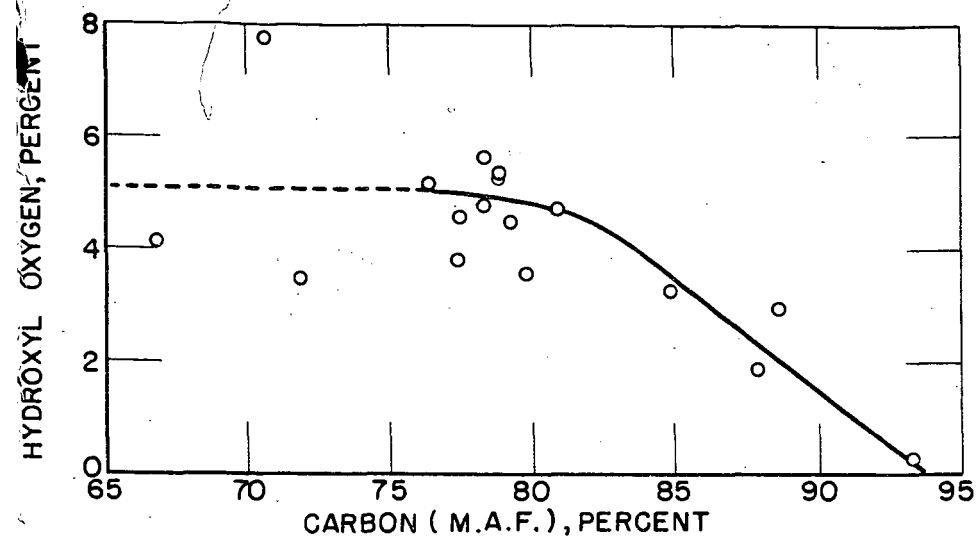


Figure 5.-Percent of hydroxyl oxygen in coals.

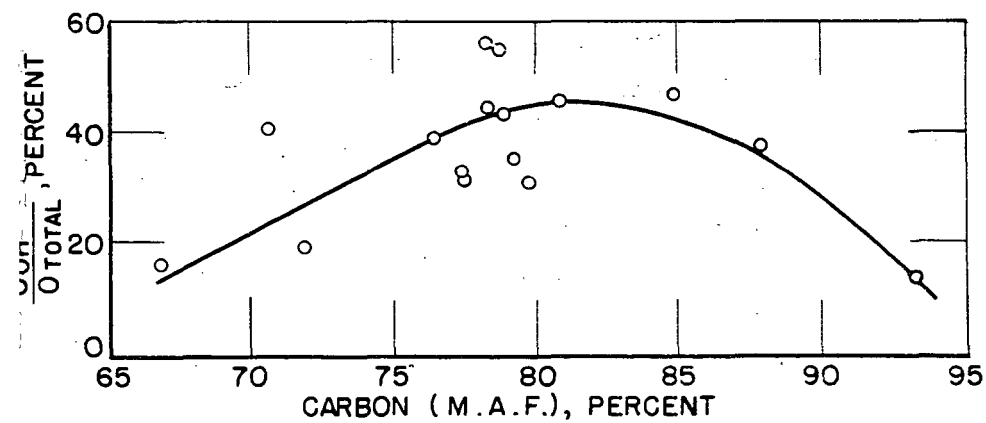


Figure 6.-Ratio of hydroxyl oxygen to total oxygen in coals.

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